

Thermal Decomposition of Aromatic Substances

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Introduction

Carefully designed experiments, allied with thermochemical kinetics analysis (1) of reaction mechanisms have led to useful working models of complex process such as hydrocarbon pyrolysis, atmospheric chemistry and combustion. A comparable understanding of even the basic chemical features of coal conversion has not yet been developed. Using a combined experimental and thermochemical kinetics approach, this work is intended to lead to effective, semiquantitative chemical models for aspects of coal pyrolysis, polymerization, hydrogenation and liquefaction.

The theoretical foundation for this research is the well-developed understanding (2) and predictive tools (1) for free radical kinetics and thermochemical estimation methods for aromatic substances (3, 4) and free radicals (5). Experiments determine rates of product evolution over as wide a range of conditions as possible with the aim of quantitative description using elementary kinetics models.

Numerous useful experiments using "model" compounds to simulate coal conversion reactions have been reported (6). The present program is not intended to simulate coal reactions, but to reveal characteristic reaction pathways in thermal aromatic chemistry and their kinetic properties, with the aim to eventually extrapolate the results to coal reactions. Two aspects of this program are reported here along with some speculations on coal chemistry.

Experimental

All liquid-phase reactions were carried out in a sealed, evacuated pyrex tube heated in an aluminum block oven. Temperature stability and accuracy were $\pm 1^\circ\text{C}$. Heat-up and cool-down times were generally negligible (< 2 min) relative to reaction duration (15 min - 48 hours). Solids were purified by recrystallization and sublimation and generally found to be 99.5+% pure by gas chromatography (gc). Tetralin was purified by distillation in a spinning band column. GC was the primary analytical tool with benzene and acetone used as solvents for reaction mixtures. Hydrogen, methane and benzene were determined via mass spectrometry. Identities of products with retention times up to that of phenanthrene were determined by coinjection on a WCOT SE-30 glass capillary column. Other products were determined on OV-101 and FFAP glass columns using temperative programming. Most kinetic analyses were carried out on packed OV-101 glass columns. A more complete account of these experiments is under preparation. The gas phase decomposition rate of 1,2 diphenylethane (12DPE) was determined using very low pressure pyrolysis methods (7).

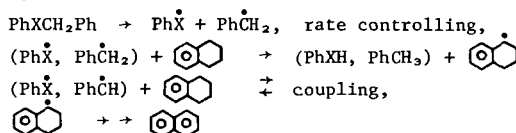
Homolytic Bond Cleavage ($\text{R-R}' \rightarrow \text{R}\cdot + \text{R}'\cdot$)

Simple cleavage of covalent bonds to generate two free radicals is commonly regarded as a major first step in coal liquefaction and pyrolysis. Therefore, it is clearly useful to be able to reliably estimate rates of bond cleavage for bonds likely to be present in coal conversion. It is possible at present to estimate rates of such cleavage in the gas-phase for a wide variety of chemical bonds using available thermodynamic and kinetic data (1, 8). While it is commonly assumed that such rate constants are roughly the same in condensed phases as in the gas-phase, this assumption has been well tested only for peroxide decomposition at $\lesssim 200^\circ$ (9).

To directly test the accuracy of the above assumption, rate constants, k_d , of bond scission for 12DPE, benzyl phenyl ether, benzyl phenyl amine and benzyl phenyl sulfide were determined in tetralin solution and compared to corresponding gas phase rate constants, k_g . As shown in Table I, the reliability of this assumption is good.

Gas phase rate constants were determined in the following manner. Very-low pressure pyrolysis was employed to find $k_g(12DPE)/s^{-1} = 2.9$ at $650^\circ C$. By assuming a central C-C bond strength of 61 kcal/mol in 12DPE (10), $\log k_g(12DPE)/s^{-1} = 14.9 - 61000/4.58 T$. For the remaining substances, k_g was estimated relative to $k_g(12DPE)$ using literature data for related compounds (11).

Liquid phase rate constants were determined in tetralin with the mole fraction of tetralin between 0.8 and 0.95. The dissociation of 12DPE was extensively studied from $325-425^\circ C$ (Figure 1), and $k_d(12DPE)/s^{-1} = 16-64800/4.58 T$. The mechanism of these reactions was consistent with the following (X = CH₂, O, NH, S):



In support of this mechanism, the disappearance of PhXCH₂Ph was first order with respect to time and independent of the initial concentration of PhXCH₂Ph. The coupling pathway was generally minor, and decreased with increasing temperature. 1,2 Dihydronaphthalene was always seen as a reaction intermediate, while 1,4-dihydronaphthalene could not be detected.

Rate constants, k , (or half-lives, $\tau_{1/2} = \ln 2/k$) for a wide variety of bond structural types can now be estimated with reasonable accuracy, and some selected examples are given in Table 3. Of special note is the prediction that under conditions where coal begins to decompose ($\sim 400^\circ C$) the only bonds to appreciably cleave are those that generate two resonance stabilized radicals.

1,2 Diphenylethane Pyrolysis

To develop an understanding of the chemistry of complex systems, it is first necessary to understand the chemistry of "simple" systems as completely and unambiguously as possible. The pyrolysis of 12DPE was chosen as a starting point for these studies since, on paper, it appeared to have a straightforward decomposition pathway, and several relevant rate constants have been measured in solution (2). A complete product analysis has been carried out at 25° intervals over the temperature range $325-450^\circ C$. Results at $375^\circ C$ for the selected products are given in Figure 2. Through analysis via thermochemical kinetics techniques and computer models the mechanism given in Figure 3 has been deduced. Some noteworthy features are:


- (1) All features of the reaction can be reasonably interpreted by a free radical scheme.
- (2) Combination of 12DPE radicals (step 3a) is favored by ≥ 3 over disproportionation (step 3b). This is similar to the behavior of the related 1-phenylethyl radical (2).
- (3) A major pathway for trans-1,2-diphenylethane (t-stilbene) production is via radical coupling (step 3a) followed by an H atom abstraction (step 4).
- (4) 1,1 diphenylethane results from an uphill ($\Delta G \sim 11$ kcal/mol) "neophyl" rearrangement (2) followed by an H-atom abstraction from 12DPE.
- (5) The formation of phenanthrene is hypothesized to occur through an unusual isomerization involving several H-atom shifts.

A set of rate constants consistent with literature values and thermochemical kinetics constraints have been deduced for this mechanism and has been found to adequately predict primary product formation rates up to $\sim 60\%$ decomposition. A

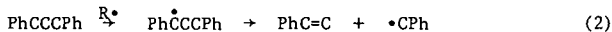
good mass balance has been achieved, and little effect on product formation upon increasing surface area has been found.

Implications for Coal Chemistry

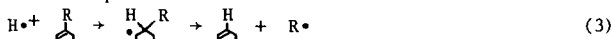
Based on experimental evidence in non-coal systems, and free radical thermochemical kinetics, certain specific features of coal conversion chemistry may be suggested.

(1) The first covalent bonds to homolytically cleave upon heating coal are those that generate two resonance stabilized radicals (e.g., benzyl radicals,  ...). In fact, under normal liquefaction conditions ($\approx 450^\circ\text{C}$) such bonds will be virtually the only bonds to break in this manner. Other reaction pathways may generate more reactive organic free radicals, however, these can be expected to abstract benzylic H-atoms, thereby producing resonance stabilized radicals. Hence, to a large extent, the free radical chemistry of coal is determined by the chemistry of resonance stabilized radicals.

(2) Modes of bond rupture other than simple bond cleavage may be very significant in coal reaction. Two well known free radical pathways, β -bond scission,

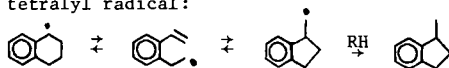


and free radical displacement



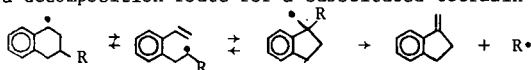
occur in 12DPE (and many other) pyrolyses. The thermal instability reported for the compounds PhCCCPH, PhCCCCPH, PhCOCC in tetralin (6b) are likely due to chain reactions involving sequence (2).

(3) In view of the relatively high temperatures and free radical concentrations (12) in coal conversion, it might be surmised that free radical isomerizations take place under coal conversion conditions which are not observed in conventional solution phase free radical experiments. In fact, the mechanism of Figure 3 contains two such reactions of the 12DPE radical in steps 5 and 6. Isomerization of tetralin and related structures has been reported by several workers. A likely path, for instance, for tetralin isomerization to 1-methyl indane (6f) is through the tetralyl radical:



Similar isomerizations can lead to structures which are thermally labile.

For instance, a decomposition route for a substituted tetralin structure in coal might be





Hence, hydroaromatic structures in coal not only act as H-donors, but may also lead to radical induced bond cleavage.

(4) The unique ability of tetralin and related compounds to act as effective donor solvents cannot be explained simply by its rate of reaction with free radicals (6d). Two other factors concerning high temperature, free radical reactions of tetralin may help explain its special solvent properties.

First, to irreversibly transfer H-atoms to radicals, the donor solvent must be transformed to a substance stable under coal conversion conditions. For instance, diphenyl methane and methyl naphthalene are effective low temperature free radical traps, however, at elevated temperatures the radicals formed upon loss of H-atoms from these molecules cannot be permanently terminated. These radicals will rapidly build up in concentration and act as H-atom acceptors from coal molecules. In support of this idea, we have found that 5:1 mixtures of diphenyl methane:12DPE at 400°C react virtually the same as does pure 12DPE at

this temperature. Despite the fact that PhCPh radicals are undoubtedly the predominant radicals in this system, these radicals will simply build up in concentration, and abstract H-atoms from 12DPE. Substances such as ethyl naphthalene and indane are also not expected to be as effective as tetralin, since their dehydrogenated molecules contain reactive styrene-like structures which may be either reduced by coal back to the starting substance, or aid in the polymerization of coal.

A second, rather unique property of tetralin-like structure is the possible reactive intermediate , in which the weak C-H bond strength is only

26 kcal/mol (5). By comparison the weakest C-H bond in  is 48 kcal/mol.

This radical will lose an H-atom which can be quite effective in depolymerizing coal through displacement reactions (e.g., 8b in Figure 3).

Conclusion

For the liquid-phase thermal decompositions studied, free radical pathways appear capable of explaining even the finest details in at least a semiquantitative manner.

In our opinion, there is no convincing evidence indicating that homogeneous coal reactions are not primarily free radical in nature. In any case, further complete studies of coal-related pyrolytic systems will indicate not only likely modes of coal reaction via free radical kinetics, but will also reveal contributions from ionic, molecular or heterogeneous pathways.

Acknowledgement

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


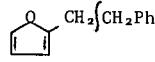
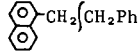
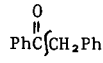

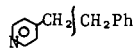
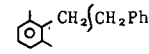
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Table I. Comparison of Dissociation Rate Constants in Gas-Phase and Liquid (tetralin)-Phase

	$\log k_g$ (est'd)/s ⁻¹	k_l (exper)/s ⁻¹ at T	k_l/k_g at T
PhCH ₂ CH ₂ Ph	15.08-61000/4.58 T	1.02 x 10 ⁻⁵ at 400°C	0.54
PhOCH ₂ Ph	15.58-52800/4.58 T	3.0 x 10 ⁻⁵ at 300°C	1.08
PhNHCH ₂ Ph	15.28-57600/4.58 T	4.4 x 10 ⁻⁵ at 375°C	0.61
PhSCH ₂ Ph	15.58-52700/4.58 T	1.04 x 10 ⁻⁵ at 300°C	0.34

Table II. Liquid Phase Bond Dissociation Rate Constants, k_l , and Half-Lives $\tau_{1/2}$ ($\theta = 4.58$ T/1000)

	$\log k_l/s^{-1}^a$	$\tau_{1/2}$ (400°C)		$\log k_l/s^{-1}$	$\tau_{1/2}$ (400°C)
	16.7-54.2/ θ^b	5 sec		16.4-61.3/ θ^d	37 min
	16.3-60.6/ θ^b	20 min	PhOCH ₂ Ph	16.4-55.0/ θ^b	20 sec
PhCH ₂ CH ₂ Ph	16.0-64.8/ θ^c	21 hr		16.0-63.3/ θ^d	69 hr
	16.0-62.2/ θ^b	3 hr		16.0-70.8/ θ^b	78 days
	16.8-57.6/ θ^d	1 min		16.0-65.8/ θ^d	44 hr
	16.0-60.8/ θ^d	1 hr			

^aUpon substitution of an alkyl group for Ph, k is reduced by $\sim 10^3$ at 400° and ~ 370 at 500°C; $k = Ae^{-E/RT}$, A is accurate to factor of 10, E is accurate ± 5 kcal/mol, k is accurate to factor of 5 (errors in A and E are correlated).

^bDerived from gas-phase data from literature (see text).

^cDerived from Figure 1. All other k values are derived from this value by correcting for differences in E and A (reference 1).

^dDerived from gas-phase data determined in our lab.

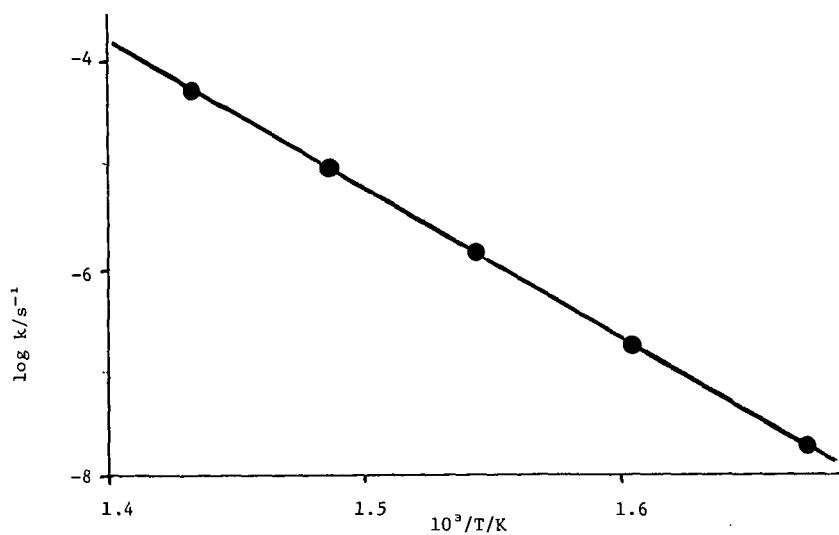


Figure 1. Arrhenius plot for 1,2 diphenylethane dissociation in tetralin

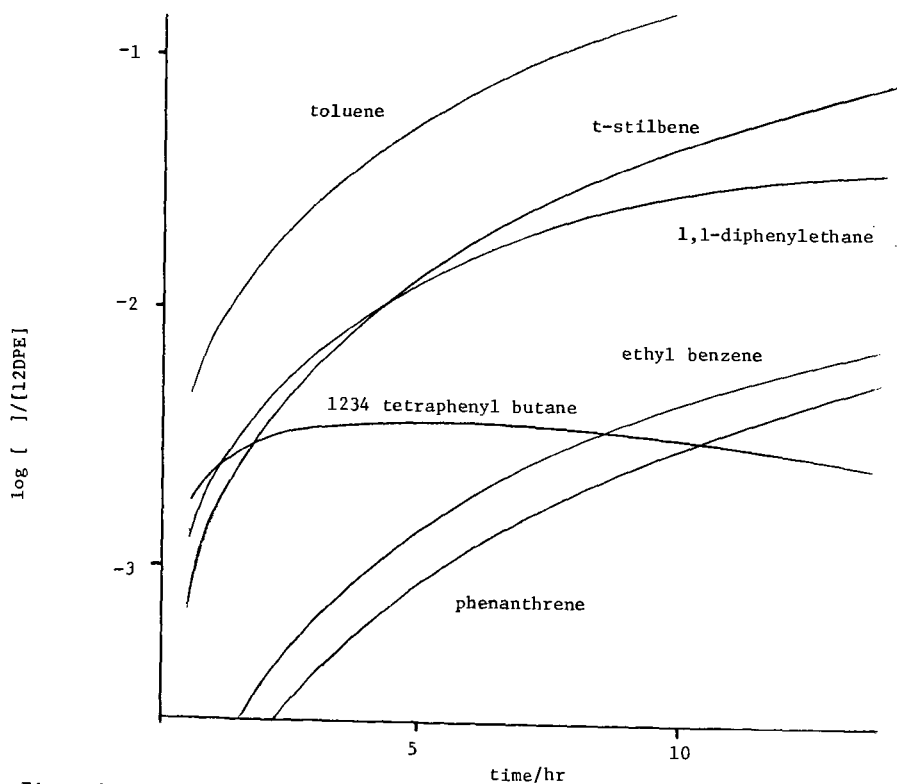
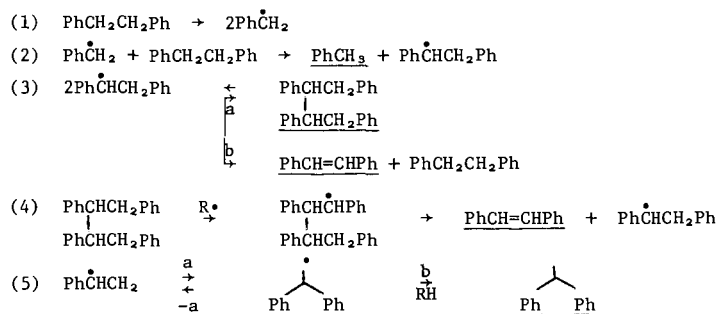


Figure 2. Product evolution in 1,2 diphenyl ethane pyrolysis at 375°C.

Figure 3. Mechanism of 1,2 diphenylethane (Ph = phenyl, R• = Ph $\dot{\text{C}}\text{HCH}_2\text{Ph}$) Pyrolysis
(Observed Products are Underlined.)

Major Pathways



Minor Pathways

